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RESEARCH IN NF COMPOUNDS (U)

By

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ABSTRACT

(U) The following phases of the program were completed and the work was assembled in the form of manuscripts: (1) Substituent Constants of Difluoraminoalkyl and Gem-bis(difluoramino)alkyl Groups, (2) Direct Fluorination of Secondary Nitronate Salts, and (3) Michael Reactions of 2-Fluoro-2,2-dinitroethanol and 2,2-Dinitropropanol with Olefinic and Acetylenic Acceptors.

(C) Nmr spectra of 2-difluoramino-2-phenylazopropane in sulfuric acid indicated initial protonation of the azo group followed by slow hydrolysis to give acetone, ammonium ion and nitrosobenzene. Spectra in fluosulfonic acid showed that a different reaction took place, possibly 1,2-shift of the phenylazo group.

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CONTRACT FULFILLMENT STATEMENT

This semiannual technical report is submitted in partial fulfillment of the contract and covers the period from 1 December 1968 through 31 May 1969.

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Introduction

(C) The objectives of this program are to develop synthesis methods for new types of high-energy compounds and to increase our understanding of the processes involved. The work is a continuation of the research that has been carried out under Contract Nonr 2655(00). In the final report periods of the latter contract*, emphasis was placed on the completion of areas of research that have been under investigation for several years, and on the preparation of manuscripts. Efforts in this direction have been continued.

(C) Three manuscripts comprise the body of this report, and some incomplete work on NF cations is presented in the appendix. The manuscript "Substituent Constants of Difluoraminoalkyl and Germ-bis(difluoramino)alkyl Groups" describes recent determinations of electronic properties of NF_2 groups. The manuscript, "Direct Fluorination of Secondary Nitronate Salts" deals with earlier fluorination work aimed mainly at starting materials for NF syntheses. For convenience 2-fluoro-2,4,4-trinitropentane (prepared under Contract N60921-67-C-0290, sponsored by the U.S. Air Force Armament Laboratory, Air Force Systems Command in collaboration with the U.S. Naval Ordnance Laboratory) and fluorodinitromethane (Aerojet-General Corp. sponsored work) are included. Likewise, portions of the paper "Michael

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* Aerojet-General Report 3672, December 1968 (Confidential)

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Reactions of 2-Fluoro-2,2-dinitroethanol and 2,2-Dinitopropanol with Olefinic and Acetylenic Acceptors" dealing with acetylene additions were carried out under Contract N60921-67-C-0290. Another manuscript describing fluorinations of amides is almost complete but additional experimental work is required to establish the fluorination path of primary amides.

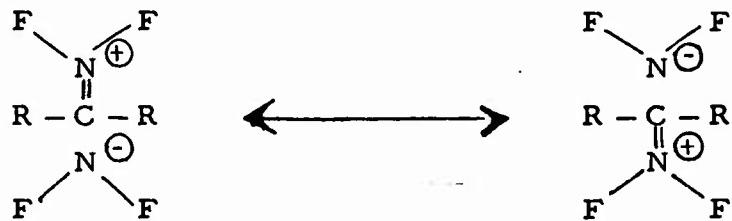
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Substituent Constants of Difluoraminoalkyl and Gem-bis(difluoramino)alkyl Groups¹

Contribution from the Environmental Systems Division,
Aerojet-General Corporation, Azusa, California

Although the difluoramino group is electron-withdrawing,² the unshared pair of electrons on nitrogen is available to support simple cations such as $\text{NF}_2\text{O}^{\oplus}$ ³ and $\text{NF}_2 = \text{NF}^{\oplus}$ ⁴ as well as difluoraminocarbonium ions.^{5,6} The operation of this effect in neutral gem-bis-difluoramino compounds could reduce the additive inductive effects by resonance structures such as the following:



The aliphatic substituent constant, σ^* , would therefore show a "saturation" effect.⁷

3-Difluoraminopropionic acid,⁵ 4,4-bis(difluoramino)pentanoic acid,⁸ and 5,5-bis(difluoramino)hexanoic acid⁸ were prepared as described previously. 4-Difluoramo-4-methylpentanoic acid was obtained by the alkaline hydrolysis of methyl 4-difluoramino-4-methylpentanoate, which, in turn, was obtained by the reaction of methyl 4-methyl-4-nitropentanoate⁹ with difluoramine in the presence of fuming sulfuric acid. Although replacement of nitro groups by difluoramine under these conditions has been used extensively

with α -halo derivatives,¹⁰ the synthesis of a tertiary alkyl difluoramino compound in this way has not been reported previously.

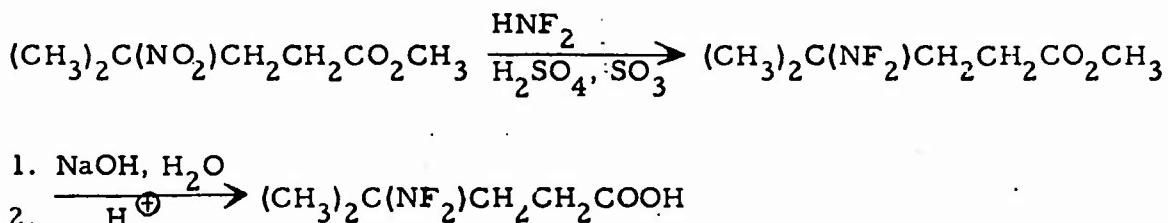


TABLE I

Ionization Constants

<u>Compound</u>	<u>pK(25°)</u>	<u>σ^*</u>	<u>$\sigma_{\text{NF}_2}^*$</u>
$\text{NF}_2\text{CH}_2\text{CH}_2\text{COOH}$	3.74	0.528	4.13
$(\text{CH}_3)_2\text{C}(\text{NF}_2)\text{CH}_2\text{CH}_2\text{COOH}$	4.35	0.174	4.84
$\text{CH}_3\text{C}(\text{NF}_2)_2\text{CH}_2\text{CH}_2\text{COOH}$	4.01	0.372	4.33
$\text{CH}_3\text{C}(\text{NF}_2)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$	4.62	-	-
$\text{CH}_3\text{C}(\text{NF}_2)_2\text{CH}_2\text{CH}_2\text{C}(\text{NO}_2)_2\text{H}$	3.87	0.381	4.42

The ionization constants of the carboxylic acids, determined by potentiometric titration,¹¹ and the corresponding σ^* values are shown in Table I. The ionization constant of 5,5-bis(difluoramino)hexanoic acid was within experimental error of that of the reference acid⁷; it was not informative as to the effect of the difluoramino groups because of the distance between functional centers. The ionization constant of 5,5-dinitro-2,2-bis(difluoramino)pentane⁸ was obtained by the spectroscopic method. The σ^* derived from the value of ρ^*

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for 1, 1-dinitroalkane ionization reported by Sitzmann, Adolph and Kamlet¹² was in agreement with that of from the corresponding carboxylic acid.

The σ^* value of the difluoramino group was calculated using the normal quenching factor of 2.8 for intervening methylene groups and the value of σ^* , for hydrogen, 0.49, to convert methyl groups to hydrogens.⁷ The value of $\sigma^*_{\text{NF}_2}$ derived from 3-difluoraminopropionic acid is considered the most reliable because only two correction factors were required.

Within the combined calculation uncertainties the σ^* values for two difluoramino groups are additive and therefore do not present evidence for unusual resonance effects. The difluoramino group is seen to be strongly electron-withdrawing, comparable with the nitro group. The reported pK for 4, 4-dinitropentanoic acid¹³ is, in fact, almost identical with that of the corresponding difluoraminoacid.

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Experimental Section

Because difluoramine and many difluoramino compounds are sensitive explosives, the safety precautions described previously⁵ were followed.

Ionization constants of the carboxylic acids were determined with a Metrohm E336 potentiograph at expanded scale by standard methods.¹¹

The reduction of 5,5,5-trinitro-2,2-bis(difluoramino)pentane with alkaline hydrogen peroxide was carried out using 1/20 the previously described quantities.⁸ The salt solution was diluted to 10 ml with water, and 1 ml aliquots were diluted with base, acid, and buffers as described by Sitzman, Adolph and Kamlet.¹² Log ϵ of the 0.1 N sodium hydroxide solution was 4.11 at λ max, 375 m μ .

Methyl 4-Difluoramino-4-methylpentanoate. — The previously described⁵ difluoramine generation procedure was followed. Methyl 4-methyl-4-nitropentanoate⁹ (5.0 g, 0.0286 mol) was added dropwise, with stirring, to 9 g of refluxing difluoramine and 8 ml of 20% fuming sulfuric acid. The mixture was quenched with 100 ml of ice 15 min after the addition was completed. The product was extracted with three 10 ml portions of methylene chloride, dried over sodium sulfate, and distilled through a 25 cm Holzmann column to give 1.30 g (25.1 % conversion, 40.5 % yield) of methyl 4-difluoramino-4-methylpentanoate, bp 56° (1.5 mm) and 1.9 g of recovered starting material.

Anal. Calcd for C₇H₁₃NF₂O₂: C, 46.43; H, 7.19; N, 7.74. Found: C, 46.50; H, 7.15; N, 7.43.

The proton nmr spectrum (CDCl₃ solution) consisted of a singlet at δ 3.80

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for OCH_3 , a triplet ($J = 1.8$ cps) at $\delta 1.32$ for $(\text{CH}_3)_2\text{CNF}_2^-$ and a multiplet at $\delta 1.7$ to 2.9 for CH_2 . The infrared spectrum showed carbonyl at 5.75μ and bands in the NF region at 10.50 (m), 10.71 (m) and 11.65μ (s).

4-Difluoramino-4-methylpentanoic Acid. — A mixture of 1.20 g (0.00663 mol) of methyl 4-difluoramino-4-methylpentanoate and 10 ml of 2.5N sodium hydroxide was heated intermittently in a 50° bath and agitated with a vortex mixer for 10 min to give a clear solution. Acidification with sulfuric acid, extraction with two 5 ml portions of ether and distillation gave 0.79 g (71.3 % yield) of 4-difluoramino-4-methylpentanoic acid, bp $72-73^\circ$ (0.05 mm).

Anal. Calcd for $\text{C}_6\text{H}_{11}\text{NF}_2\text{O}_2$: C, 43.11; H, 6.60; N, 8.39. Found: C, 42.84; H, 6.41; N, 7.95.

The proton nmr spectrum (CDCl_3 solution) consisted of a singlet at $\delta 11.02$ for $-\text{COOH}$, a triplet ($J = 2$ cps) at $\delta 1.30$ for CH_3 and a multiplet at $\delta 1.8$ to 2.9 for CH_2 .

Acknowledgment. — The author is grateful to Mrs. Yoschie Kadota for the pK determinations of the carboxylic acids, to Mr. K. Inouye for elemental analysis and Dr. W. Woolfenden for nmr spectra.

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Direct Fluorination of Secondary Nitronate Salts¹

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Contribution from the Environmental Systems Division,
Aerojet-General Corporation, Azusa, California

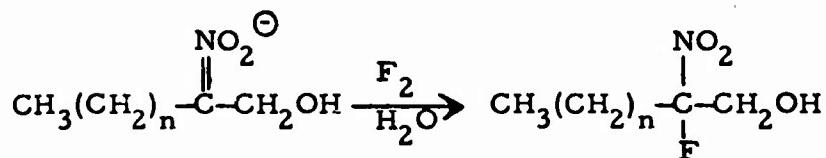
1-Fluoro-1,1-dinitroalkanes are readily prepared by the direct fluorination of aqueous solutions of nitronitronate salts.^{2, 3, 4} Simple primary^{2, 5} and secondary⁵ gem-fluoronitro compounds, α -fluoro- α -nitroketones and nitriles,⁵ as well as 2-fluoro-2-nitromalonates and cyanoacetates⁶ were also prepared from the corresponding nitronate salts. Also, fluorinations of suspensions of the salt of 2,2-dimethyl-5-nitro-1,3-dioxane in carbon tetrachloride⁷ and of aqueous solutions of the salt of 2-nitro-1,3-propanediol⁸ were reported to give 5-fluoro-2,2-dimethyl-5-nitro-1,3-dioxane and 2-fluoro-2-nitro-1,3-propanediol, respectively.

Salts of simple 2-nitroalcohols were found to undergo direct fluorination in aqueous solution. In this way 2-fluoro-2-nitrobutanol, 2-fluoro-2-nitropentanol, 2-fluoro-2-nitrohexanol and 2-fluoro-2-nitroheptanol were synthesized in yields of 21 to 42.5%. As in the fluorinations of other mononitro salts, an acid-forming side reaction resulted in the liberation of unfluorinated nitro compounds, but the boiling points of these differed sufficiently from those of the products to allow isolation by fractional distillation.

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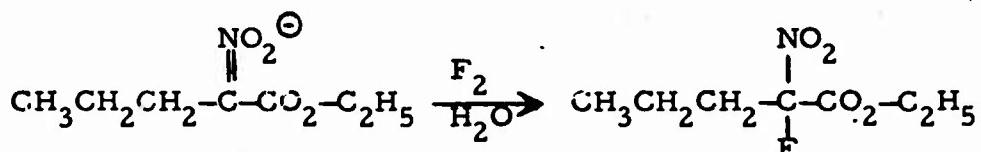
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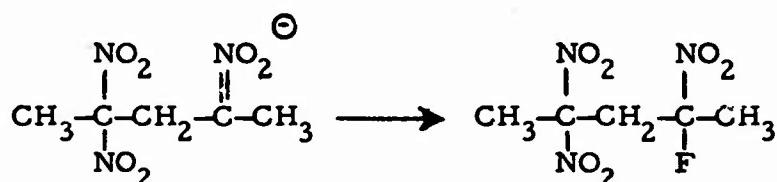


$n = 1, 2, 3, 4$

The activating effect of a single carboalkoxy group was demonstrated using ethyl-2-nitropentanoate. The fluorination of the nitronate salt gave ethyl-2-fluoro-2-nitropentanoate in 85% yield (54.5% conversion).



Sodium 4,4-dinitro-2-pantanenitronate available in connection with another study⁹ was also fluorinated, and 2-fluoro-2,4,4-trinitropentane was isolated in 11.5% yield. In this case column chromatography was used to isolate the product.

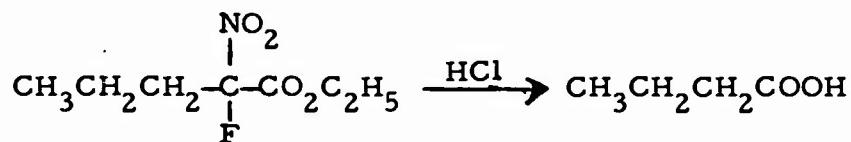


Since 2-nitroalcohols and 2-nitroacids readily undergo deformylation and decarboxylation, respectively, the fluoro derivatives could be expected to serve as convenient precursors to 1-fluoro-1-nitroalkanes. One must bear in mind, however, that α -fluorines have been shown to decrease the acidity of substituted nitromethanes,¹⁰ and this destabilization of nitronate

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Chlorofluoronitroacetate esters have been reported to yield chlorofluoronitromethane at ambient temperature on reaction with diethylamine¹¹ or water.⁵ Ethyl 2-fluoro-2-nitropentanoate however, was unreactive under these conditions, or with refluxing diethylamine or aqueous sodium hydroxide solution at 0°. Refluxing aqueous sodium hydroxide gave a complex mixture of degradation products, whereas refluxing 18% hydrochloric acid gave a quantitative yield of butyric acid.



Infrared and nmr spectra of the new compounds are described in the Experimental Section. An unusual feature of the proton spectra of the fluoronitroalcohols and 2-fluoro-2,4,4-trinitropentane is that methylenes adjacent to fluoronitro groups have the appearance of a singlet and an AB quartet of 1 H area each. The methylene hydrogens are nonequivalent because of the adjacent assymmetric center and the observed ABX profile can result¹² from equality of the difference in chemical shifts to 1/2 ($J_{AX} - J_{BX}$).

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Experimental Section

General. — Fluorinations were carried out in glass apparatus as described previously.² The fluorine was diluted fourfold to sixfold with nitrogen.

2-Fluoro-2-nitrobutanol. — A solution of 230 g (1.93 mol) of 2-nitrobutanol and 85.1 g (2.12 mol) of sodium hydroxide in 4 liters of water was treated with 2 mol of fluorine at 5 to 10° over a 2 hr period. The solution was saturated with sodium chloride and was extracted with five 400 ml portions of methylene chloride. The methylene chloride solution was dried over sodium sulfate and distilled through a 10 cm Vigreauz column to give 110 g of impure 2-fluoro-2-nitrobutanol, bp 57 to 60° (0.8 mm), and 37 g of 2-nitrobutanol, bp 65 to 72° (0.8 mm). Redistillation gave 91.3 g (34.5% conversion, 42.5% yield) of 2-fluoro-2-nitrobutanol, bp 102-104° (13 mm). A total of 43 g of starting material was recovered.

Anal. Calcd for C₄H₈NO₃F: C, 35.04; H, 5.84; N, 10.22. Found: C, 34.90; H, 5.90; N, 10.11.

The fluorine nmr spectrum (CCl₄ solution) consisted of a symmetrical multiplet at δ^* 139.8. The proton spectrum consisted of a triplet for the methyl at δ 1.01 ($J = 7.5$ cps), a multiplet for the methylene of the ethyl group at δ 2.23, a broad singlet at δ 3.0 shifted by dilution for the hydroxyl, and the AB portion of an ABX pattern for -CH₂OH ($\delta_A = 4.00$, $\delta_B = 4.14$, $J_{AB} = 14.0$ cps, $J_{AX} = 26.2$ cps, $J_{BX} = 9.8$ cps). Prominent infrared bands were 3.0, 6.40, 9.3 and 12.0 μ .

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2-Fluoro-2-nitropentanol.--A solution of 102 g (0.99 mol) of 1-nitrobutane, 40 g (1.0 mol) of sodium hydroxide and 84 g (1.0 mol) of formalin in 1250 ml of water was treated with 1 mol of fluorine. The product was isolated as above, but using a 25 cm Holzmann column for the distillation to give 31.0 g (21% yield) of 2-fluoro-2-nitropentanol, bp 29-30° (0.025 mm).

Anal. Calcd for $C_5H_{10}NO_3F$: C, 39.74; H, 6.67; N, 9.27. Found: C, 39.71; H, 6.63; N, 9.40.

The fluorine nmr spectrum (CCl_4 solution) consisted of a multiplet at ϕ^* 138.1 with a profile identical with that of 2-fluoro-2-nitrobutanol. The proton spectrum consisted of a triplet ($J = 7$ cps) at δ 1.00 for the methyl, multiplets at δ 1.5 and 2.1 for the propyl methylenes, a broad singlet at δ 3.3 for the hydroxy, and the AB portion of an ABX pattern for the carbinol protons ($\delta_A = 4.12$, $\delta_B = 3.98$, $J_{AB} = 13.8$, $J_{AX} = 25.1$, $J_{BX} = 10.4$). Prominent infrared bands were 2.9, 6.40, 9.18 and 11.85 μ .

2-Fluoro-2-nitrohexanol.--The fluorination of a solution of 52.0 g (0.445 mol) of nitropentane, 17.8 g (0.445 mol) of sodium hydroxide and 37.4 g (0.445 mol) of formalin in 600 ml of water by the above procedure gave 21.2 g (28.4%) of 2-fluoro-2-nitrohexanol, bp 42-43° (0.025 mm).

Anal. Calcd for $C_6H_{12}NO_3F$: C, 43.63; H, 7.33; N, 8.45. Found: C, 43.67; H, 7.51; N, 8.13.

The fluorine nmr spectrum consisted of a multiplet at ϕ^* 138.2. The proton spectrum (pyridine solution) consisted of a triplet ($J = 6.1$ cps) at δ 0.77 for the methyl, multiplets at δ 1.3 and 2.2 for the butyl methylenes, and the AB portion of an ABX pattern for the carbinol protons ($\delta_A = 4.52$,

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$\delta_B = 4.35$, $J_{AB} = 13.4$ cps, $J_{AX} = 30.4$ cps, $J_{BX} = 9.7$ cps). Prominent infrared bands were 2.9, 6.40, 9.1, and 11.85 μ .

2-Fluoro-2-nitroheptanol.—The above procedure with 60 g (0.457 mol) nitrohexane gave 20.0 g (24.5%) of analytically pure 2-fluoro-2-nitroheptanol. Two redistillations were required to remove 2-nitroheptanol.

Anal. Calcd for $C_7H_{14}NO_3F$: C, 46.93; H, 7.82; N, 7.82. Found: C, 46.76; H, 7.97; N, 7.47.

The fluorine nmr spectrum (pyridine solution) consisted of a multiplet at δ^* 137.7. The proton spectrum showed a triplet ($J = 4.9$ cps) at δ 0.82 for the methyl, multiplets at δ 1.2 and 2.3 for the pentyl methylenes, and the AB portion of an ABX pattern for the carbinol methylene ($\delta_A = 4.35$, $\delta_B = 4.52$, $J_{AB} = 13.8$ cps, $J_{AX} = 30.3$ cps, $J_{BX} = 9.8$ cps). Prominent infrared bands were 2.95, 6.40, 9.1, 9.4 and 11.88 μ .

Ethyl 2-Fluoro-2-nitropentanoate.—A solution of 160 g (0.91 mol) of ethyl 2-nitropentanoate¹³ and 1.0 mol of sodium hydroxide in 2 liters of water was fluorinated at 0 to 5° with 1 mol of fluorine. The product was extracted with methylene chloride, dried over sodium sulfate and distilled through a 25 cm Holzmann to give 96 g (54.5% conversion, 85% yield) of ethyl 2-fluoro-2-nitropentanoate, bp 36° (0.35 mm) and 57.5 g (0.33 mol) of recovered ethyl 2-nitropentanoate, bp 39° (0.025 mm).

Anal. Calcd for $C_7H_{12}NO_4F$: C, 43.49; H, 6.26; N, 7.25. Found: C, 43.48; H, 6.03; N, 7.14.

The proton nmr spectrum (CCl_4 solution) consisted of a quartet

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($J = 5.4$ cps) at $\delta 4.3$ for the ethoxy methylene, a doublet ($J_{HF} = 20$ cps) of triplets ($J = 7$ cps) at $\delta 2.40$ for $\text{CH}_2-\text{CFNO}_2-$, and a triplet at $\delta 1.30$ for the ethoxy methyl superimposed over a methylene multiplet near $\delta 1.30$ and a distorted triplet ($J = 6.4$ cps) at $\delta 0.98$ methyl. The fluorine spectrum consisted of a broadened triplet ($J = 20.8$ cps) at $\phi^* 125.2$. The infrared spectrum showed a carbonyl band at 5.74μ and a nitro band at 6.43μ .

2-Fluoro-2,4,4-trinitropentane. -- 2-nitropropene (4.35 g, 0.050 mol) was added dropwise with stirring to a solution of 6.0 g (0.050 mol) of 1,1-dinitroethane in 40 ml of 1.25 N sodium hydroxide at 0 to 10° . The resulting suspension of sodium 4,4-dinitro-2-pantanenitronate⁸ was fluorinated at 0 to 5° with 0.05 mol of fluorine. The product was extracted with 80 ml of methylene chloride, dried over sodium sulfate and distilled to give 4.9 g of liquid, bp $80-110^\circ$ (0.2 mm). Column chromatography, using a 35 x 220 mm column of neutral active alumina and ethyl ether gave 0.1 g of residue from the first 300 ml of eluent, 1.30 g from the next 50 ml and subsequently only 0.08 g. The 1.30 g fraction was identified as 2-fluoro-2,4,4-trinitropentane (11.5% yield overall), bp 53° (0.025 mm).

Anal. Calcd for $\text{C}_5\text{H}_8\text{N}_3\text{FO}_6$: C, 26.67; H, 3.55; N, 18.67; F, 8.45.
Found: C, 26.97; H, 3.28; N, 18.11; F, 8.51.

The infrared spectrum consisted of peaks at 3.31 (w), 3.36 (w), 3.43 (w), 6.37 (vs), 6.90 (m), 7.17 (s), 7.30 (m), 7.40 (m), 7.57 (s), 8.06 (s), 8.5 (m), 8.66 (m), 11.4 (w) and 11.80μ (s).

The fluorine nmr spectrum (no solvent) consisted of a symmetrical

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multiplet at ϕ^* 122.5. The proton spectrum consisted of doublet ($J = 21$ cps) at δ 2.07 for $-CF(NO_2)_2CH_3$, a singlet at δ 2.75 for $-C(NO_2)_2CH_3$, and an ABX pattern for the methylene ($J_{AX} = 22.8$ cps, $J_{BX} = 7.5$ cps, $J_{AB} = 16.5$ cps, $\delta_A = 3.78$, $\delta_B = 3.67$).

1-Bromo-1-fluoro-1-nitropropane.—To a freshly prepared solution at 10° of 1.25 mol of bromine and 2.50 mol of sodium hydroxide in 1500 ml of water, 68.6 g (0.50 mol) of 2-fluoro-2-nitrobutanol was added over a 10 min period, and the mixture was allowed to stand for 30 min at 10° . The product was extracted with three 100 ml portions of methylene chloride, dried over sodium sulfate, and distilled through a 25 cm Holzmann column to give 30.0 g (32% conversion, 56.5% yield) of 1-bromo-1-fluoro-1-nitropropane, bp 90° (47 mm) and 22.4 g of recovered 2-fluoro-2-nitrobutanol.

Anal. Calcd for $C_3H_5NO_2BrF$: C, 19.37; H, 2.69; N, 7.53. Found: C, 19.37; H, 2.72; N, 7.63.

The proton nmr spectrum consisted of a triplet ($J = 7.3$ cps) at δ 1.1 for the methyl and a doublet of quartets ($J_{HF} = 18$ cps, $J_{HH} = 7.3$ cps) at δ 2.8 for the methylene. The fluorine spectrum consisted of a distorted triplet ($J = 18.5$ cps) at ϕ^* 85.6. The infrared spectrum consisted of peaks at 3.32 (w), 3.36 (w), 3.41 (w), 6.32 (s), 6.84 (m), 6.98 (m), 7.2 (w), 7.41 (s), 7.5 (s), 7.79 (s), 8.30 (s), 8.90 (s), 9.30 (s), 9.50 (w), 10.00 (s), 10.50 (s), 10.60 (s), 11.30 (m), 11.70 (w), 12.30 (s), 12.9 (sh), and 13.11 (m).

Fluorodinitromethane.—A solution of 100 g (0.65 mol) of 2-fluoro-2,2-dinitroethanol in 280 ml of concentrated sulfuric acid and 165 ml of water

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was added with stirring, over a 30 min period, to a solution of 400 g (1.34 mol) of sodium dichromate dihydrate in 800 ml of water at 25 to 40°. The solution was allowed to stand at ambient temperature for 66 hrs and was then extracted with three 300 ml portions of methylene chloride. Distillation through a 25 cm Holzmann column gave 38 g (47% conversion, 63% yield) of fluorodinitromethane,³ bp 40° (20 mm) and 19.0 g of 2-fluoro-2,2-dinitroethanol, bp 38-39° (0.1 mm). An additional 6.2 g of 2-fluoro-2,2-dinitroethanol was recovered by diluting the aqueous layer with an equal volume of water and extracting with ether.

Oxidation of 2-Fluoro-2-nitroheptanol. — 2-Fluoro-2-nitroheptanol (4.0 g, 0.022 mol) was added to a solution of 20 g of sodium dichromate dihydrate and 14 ml of concentrated sulfuric acid in 48 ml of water. After 3 days, the solution was diluted with an equal volume of water and was extracted with three 50 ml portions of methylene chloride. Distillation gave 1.92 g (75% yield) of caproic acid, bp 65° (1 mm).

Reaction of Ethyl 2-Fluoro-2-nitropentanoate with Diethylamine. — A solution of 1.93 g (0.010 mol) of ethyl 2-fluoro-2-nitropentanoate in 2 g of diethylamine was allowed to stand for 24 hrs at ambient temperature. Distillation gave 1.47 g (76%) of unchanged starting material. Refluxing a solution of 1 g of the ester in 5 g of diethylamine for 2 hrs resulted in the isolation of only starting material.

Reaction of Ethyl 2-Fluoro-2-nitropentanoate with Hydrochloric Acid. — A mixture of 1.93 g (0.010 mol) of ethyl 2-fluoro-2-nitropentanoate, 15 ml of concentrated hydrochloric acid and 15 ml of water was refluxed for 2.5 hrs.

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The solution was saturated with sodium chloride and extracted with three 15 ml portions of methylene chloride. Distillation gave 0.85 g (97% yield) of butyric acid. bp 164°.

Acknowledgment. — The author is indebted to Mr. K. Inouye for elemental analysis, to Mr. L. A. Maucieri and Dr. W. R. Woolfenden for nmr analysis and to Mr. H. F. Shuey for assistance in the synthesis work.

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Michael Reactions of 2-Fluoro-2,2-dinitroethanol and 2,2-Dinitopropanol with Olefinic and Acetylenic Acceptors¹

Vytautas Grakauskas and Kurt Baum

Contribution from the Environmental Systems Division,
Aerojet-General Corporation, Azusa, California

ABSTRACT

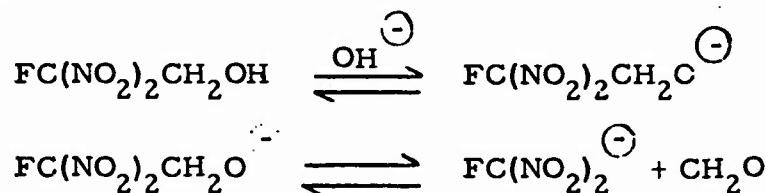
Michael reactions of 2,2-dinitroalcohols were found to take place with or without prior deformylation, depending on the reaction condition and the nature of the acceptor. Reactions of 2-fluoro-2,2-dinitroethanol with ethyl acrylate, methyl vinyl ketone, and acrylonitrile in aqueous alkali, gave ethyl 4-fluoro-4,4-dinitrobutyrate, 5-fluoro-5,5-dinitro-2-pentanone, and 4-fluoro-4,4-dinitrobutyronitrile, respectively. The reaction of 2-fluoro-2,2-dinitroethanol with ethyl propionate catalyzed by pyridine gave cis and trans ethyl β -(2-fluoro-2,2-dinitroethoxy)acrylate, whereas the reaction in aqueous alkali gave these compounds as well as cis and trans ethyl 3-fluoro-3,3-dinitrocrotonate. Dimethyl acetylenedicarboxylate and 2-fluoro-2,2-dinitroethanol gave only diethyl 2-fluoro-2,2-dinitroethoxyfumarate with pyridine catalysis, and both the fumarate and maleate with aqueous alkali. The pyridine catalyzed reaction of 2,2-dinitopropanol with ethyl propionate gave ethyl α -(2,2-dinitropoxy)acrylate; in aqueous solution, the salt of 1,1-dinitroethane and ethyl propionate gave ethyl 4,4-dinitropentenoate.

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1, 1-Dinitroalkanes undergo the Michael reaction with α , β -olefinic esters, nitriles, aldehydes and ketones. 2, 2-Dinitroalcohols, which are readily deformed in the presence of base, give Michael adducts of the corresponding 1, 1-dinitroalkanes.² Limited work has been done with acetylenic acceptors; 1:1 Michael adducts were reported for reactions of 1, 1-dinitroalkanes with methyl propiolate³ and for reactions of nitroform with propionic acid and amide.⁴ The synthesis of 2-fluoro-2, 2-dinitroethanol has been reported recently,^{5, 6} and Michael reactions of this unusual nitroalcohol have now been examined. Because of the reported destabilization of nitronate anions by α -fluorines,⁷ a significant concentration of fluorodinitroethoxide ion could be expected with the following equilibria operating in the presence of base:



Inasmuch as simple alcohols have been reported to form 1, 4-adducts with acrylates,⁸ acrylonitrile,⁹ and methyl vinyl ketone¹⁰ in the presence of base, 2-fluoro-2, 2-dinitroethanol could be expected to yield 2-fluoro-2, 2-dinitroethyl ethers or fluorodinitromethane derivatives.

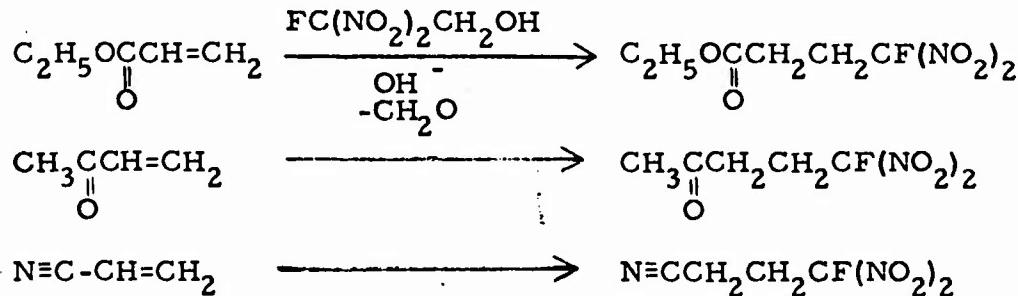
Ethyl acrylate, methyl vinyl ketone, and acrylonitrile were found to react with 2-fluoro-2, 2-dinitroethanol in aqueous alkaline solution to give ethyl 4-fluoro-4, 4-dinitrobutyrate, 5-fluoro-5, 5-dinitro-2-pentanone, and 4-fluoro-4, 4-dinitrobutyronitrile, respectively. Thus either the alkoxide ion did not react with these olefins or the addition was reversible and the

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fluorodinitromethane adducts were more stable under the conditions.



Pyridine has been reported to effect the acylation of 2,2-dinitro-alcohols without causing deformylation.¹¹ The above conjugated olefins, however, did not react with 2-fluoro-2,2-dinitroethanol in the presence of pyridine. The stronger base, triethylamine, resulted in a very slow reaction of 2-fluoro-2,2-dinitroethanol with methyl acrylate, but only with deformylation to give methyl 4-fluoro-4,4-dinitrobutyrate.

The reverse Michael reaction is most likely to occur when the forward reaction is slow.¹² Consequently, the high reactivity of activated acetylenic compounds toward nucleophiles¹³ should enhance the probability of isolating the primary adducts with this class of acceptor. Therefore, reactions of 2-fluoro-2,2-dinitroethanol with ethyl propionate and with dimethyl acetylenedicarboxylate were investigated.

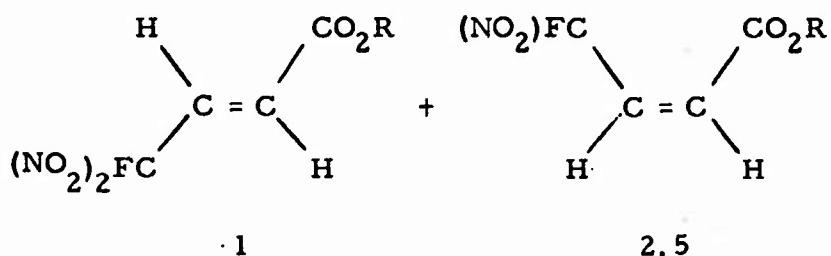
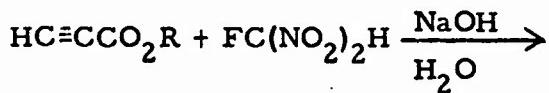
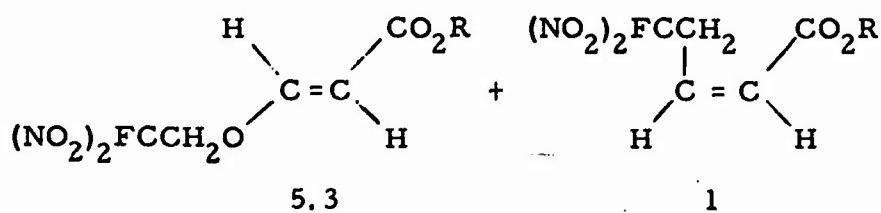
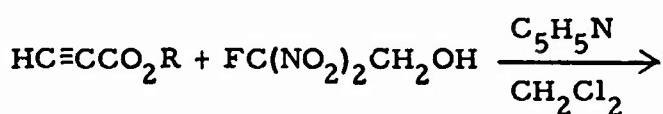
The reaction of 2-fluoro-2,2-dinitroethanol with ethyl propionate in methylene chloride solution, catalyzed by pyridine, gave ethyl -(2-fluoro-2,2-dinitroethoxy)acrylate in 76% yield. Nmr spectra showed that the product was a mixture of trans and cis isomers in the ratio 5.3:1. The olefinic hydrogen chemical shifts and coupling constants ($J_{cis} = 7.5$ cps, $J_{trans} = 12.6$ cps) corresponded with those reported for other β -alkoxyacrylates¹⁴ ($J_{cis} = 7$ cps,

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$J_{trans} = 12.5$ cps). Details of the spectra are given in the Experimental Section.

When the reaction of ethyl propiolate with 2-fluoro-2,2-dinitroethanol was carried out in aqueous alkaline solution, both ethyl β -(2-fluoro-2,2-dinitroethoxy)acrylate and ethyl 3-fluoro-3,3-dinitrocrotonate were isolated. The latter product was also prepared from fluorodinitromethane and ethyl propiolate under the same conditions, and the ratio of trans to cis isomers was 1:2.5

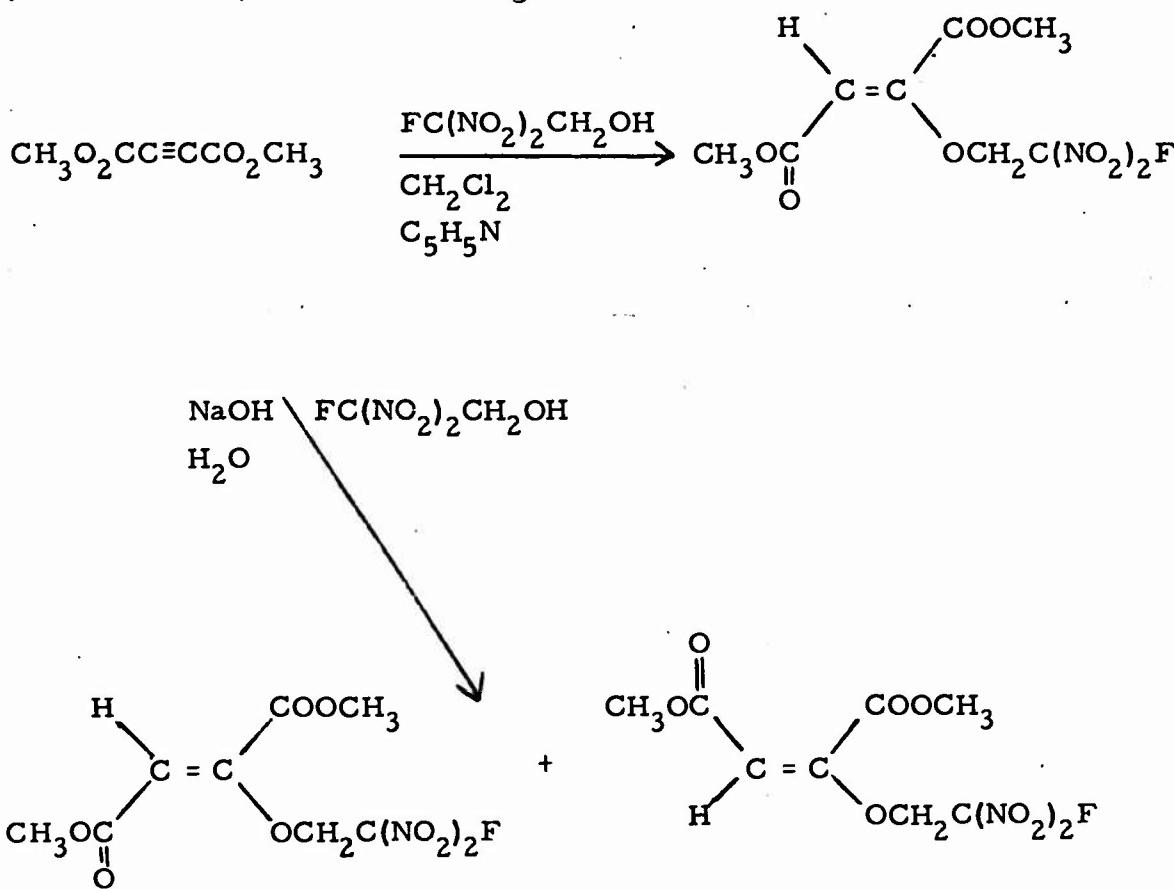


With dimethyl acetylenedicarboxylate, only alkoxide addition without

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deformylation was observed. The reaction with 2-fluoro-2,2-dinitroethanol in methylene chloride catalyzed by pyridine gave an 88% yield of dimethyl 2-fluoro-2,2-dinitroethoxyfumarate, and the maleate was not detected. When this reaction was conducted in aqueous sodium hydroxide, both isomers were obtained in the ratio 3:1, respectively. In this case, the combined yield was only 11%, and the major product was a nonvolatile oil with elemental analysis identical with the above esters. Comparison of the chemical shifts of the olefinic protons (δ 6.41 for the fumarate, δ 5.6 for the maleate) with values reported¹⁴ for other alkoxyfumarates (δ 6.1 to 6.45) and alkoxymaleates (δ 5.05 to 5.15) was used to assign the isomeric structures.



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To determine whether polynitroalcohols that deformylate more readily than 2-fluoro-2,2-dinitroethanol can also give direct adducts with activated acetylenes, the reaction of 2,2-dinitropropanol with ethyl propiolate was investigated. Using methylene chloride as solvent and pyridine as catalyst gave ethyl β -(2,2-dinitropoxy)acrylate in 79% yield with a ratio of trans to cis isomers of 3.4:1. This is the first example of the Michael addition without prior deformylation of a 2,2-dinitroalkanol, and shows that the alcohol is not deformylated under these conditions. The reaction 1,1-dinitroethane with ethyl propiolate in aqueous base, on the other hand, gave ethyl 4,4-dinitro-2-pentenoate with a trans to cis ratio of 1:3.

With the exceptions of the pyridine-catalyzed additions to ethyl propiolate, all of these reactions with activated acetylenes took place predominately by trans additions. Winterfeldt and Preuss¹⁴ also observed predominately trans addition in reactions of alcohols with dimethyl acetylene-dicarboxylate catalyzed by tertiary amines, and cis additions with methyl propiolate.

The formation of fluorodinitroethyl ethers in Michael reactions of 2,2-dinitroethanol in aqueous solution confirms the presence of an appreciable amount of 2-fluoro-2,2-dinitroethoxide ion in the equilibria. The course of the reaction is influenced by the reactivity of the acceptor. The most reactive acceptor used in this work, dimethyl acetylenedicarboxylate, gave only ethers, whereas ethyl propiolate gave addition with deformylation as well, and the olefinic acceptors gave only deformylation products. Nonaqueous pyridine-catalyzed reactions gave no evidence of deformylation, and yielded ethers with the more reactive acceptors only.

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EXPERIMENTAL SECTION

Caution - Safety shielding should be used in work with fluorodinitro compounds. 2-Fluoro-2,2-dinitroethanol is a severe skin irritant, and contact should be avoided.

Ethyl 4-Fluoro-4,4-dinitrobutyrate.- Ethyl acrylate (2.0 g, 0.020 mol) was added dropwise with stirring over a 5 min period to a solution of 2.0 g of potassium hydroxide and 3.1 g (0.020 mol) of 2-fluoro-2,2-dinitroethanol⁶ in 30 ml of water at 10 - 15°. After 5 min, the product was extracted with 25 ml of methylene chloride and distilled to give 2.5 g (56% yield) of ethyl 4-fluoro-4,4-dinitrobutyrate, bp 67 - 68° (0.1 mm), n_D^{25} 1.4280.

Anal. Calcd for $C_6H_9FN_2O_6$: C, 32.1; H, 4.0; N, 12.5; F, 8.5.
Found: C, 31.8; H, 3.7; N, 12.3; F, 8.3.

The proton nmr spectrum in carbon tetrachloride displayed a multiplet between δ 3.5 and δ 2.9 for the β-methylene, a triplet at δ 2.6 for the α-methylene, and a quartet at δ 4.2 and a triplet at δ 1.3 for the ethyl group. The fluorine nmr spectrum exhibited a triplet at δ^* 104.9, $J_{HF} = 17$ cps.

Methyl 4-Fluoro-4,4-dinitrobutyrate.- Triethylamine, 4.0 g (0.040 mol) was added dropwise with stirring at 28 - 32° to a solution of 6.24 g (0.040 mol) of 2-fluoro-2,2-dinitroethanol and 3.44 g (0.040 mol) of methyl acrylate in 50 ml of methylene chloride, and the resulting solution was allowed to stand at 25° for seven days. The dark reaction mixture was washed with 100 ml of 1% sulfuric acid and was distilled to give 3.2 g (38% yield) of methyl 4-fluoro-4,4-dinitrobutyrate, bp 53° (0.05 mm) n_D^{25} 1.4310.

Anal. Calcd for $C_5H_7N_2FO_6$: C, 28.6; H, 3.3; N, 13.3; F, 9.0.
Found: C, 28.3; H, 3.6; N, 12.7; F, 9.1.

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5-Fluoro-5,5-dinitro-2-pentanone - A solution of 1.0 g of potassium hydroxide in 30 ml of water was added at 20° with stirring to a solution of 4.6 g (0.030 mol) of 2-fluoro-2,2-dinitroethanol and 2.1 g (0.030 mol) of methyl vinyl ketone in 70 ml of water. After 40 min, the product was extracted with 40 ml of methylene chloride, and distilled to give 3.5 g (72% yield) of a pale yellow liquid, bp 71 - 72° (0.1 mm), n_D^{25} 1.4355.

Anal. Calcd for $C_5H_9N_2FO_5$: C, 30.6; H, 4.6; N, 14.3; F, 9.7.
Found: C, 30.3; H, 4.4; N, 14.0; F, 9.6.

The proton nmr spectrum in carbon tetrachloride consisted of a superposition of a doublet of triplets and an AB pattern at δ 2.7 to 3.5 for the methylenes and a singlet at δ 2.2 for the methyl. The fluorine spectrum exhibited a triplet ($J = 15$ cps) at ϕ^* 104.2.

4-Fluoro-4,4-dinitrobutyronitrile - A solution of 1.8 g (0.045 mol) of sodium hydroxide in 20 ml of water was added at 25° with stirring to a solution of 2.1 g (0.040 mol) of acrylonitrile and 6.2 g (0.040 mol) of 2-fluoro-2,2-dinitroethanol in 40 ml of water. After 20 min, the product was extracted with 25 ml of methylene chloride and distilled to give 2.0 g (28% yield) of 4-fluoro-4,4-dinitrobutyronitrile, bp 88-89° (0.1 mm), n_D^{25} 1.4440.

Anal. Calcd for $C_4H_4N_3FO_4$: C, 27.1; H, 2.3; N, 23.7; F, 10.7.
Found: C, 26.7; H, 2.5; N, 23.2; F, 11.2.

The proton nmr spectrum (CCl_4 solution) showed a triplet ($J = 6.3$ cps) at δ 2.74 for the α -methylene and a doublet of triplets ($J_{HF} = 18$ cps, $J_{HH} = 6.3$ cps), at δ 3.18 for the β -methylene.

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Ethyl β -(2-Fluoro-2,2-dinitroethoxy)acrylate - To a solution of 15.8 g (0.20 mol) of pyridine in 150 ml of methylene chloride was added dropwise with stirring, at 5 - 7° a mixture of 15.4 g (0.10 mol) of 2-fluoro-2,2-dinitroethanol and 9.8 g (0.10 mol) of ethyl propiolate. The reaction mixture was allowed to stand at room temperature for 18 hrs and the resulting black solution was washed with a cold solution of 22 g of sulfuric acid in 120 ml of water. Removal of the solvent and molecular distillation of the residue at 98 - 101°(0.025 mm) gave 19.2 g (76% yield) of colorless liquid, n_D^{25} 1.4575.

Anal. Calcd for $C_7H_9N_2FO_7$; C, 33.3; H, 3.6; N, 11.1; F, 7.5.
Found: C, 33.3; H, 3.8; N, 10.9; F, 7.5.

The nmr spectra ($CDCl_3$ solution) were consistent with a 5.3:1 ratio of trans- to cis- ethyl β -(2-fluoro-2,2-dinitroethoxy)acrylate. The proton spectrum showed a triplet at δ 1.2 and quartets at δ 4.30 (trans) and δ 4.25 (cis) for the ethoxy groups, overlapping doublets ($J_{HF} = 16.4$ cps) at δ 5.3 for the fluorodinitroethoxy groups, trans olefinic doublets ($J_{HH} = 12.6$ cps) at δ 7.7 and 5.6, and cis olefinic doublets ($J_{HH} = 7.5$ cps) at δ 6.8 and 5.07. The fluorine spectrum showed a triplet ($J = 16$ cps) at ϕ^* 109.4.

When this reaction was carried out in aqueous solution, a mixture of ethyl 3-fluoro-3,3-dinitrocrotonate and ethyl β -(2-fluoro-2,2-dinitroethoxy)-acrylate was obtained. A mixture of 7.7 g (0.050 mol) of 2-fluoro-2,2-dinitroethanol and 4.9 g (0.050 mol) of ethyl propiolate was added dropwise with stirring over a period of 10 min at 0-5° to a solution of 2.4 g (0.060 mol) of sodium hydroxide in 100 ml of water. The reaction mixture was kept at 0-3° for 1.5 hrs, and at 18 - 20° for 45 min. Extraction with 50 ml of

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methylene chloride and distillation gave 1.2 g of ethyl 3-fluoro-3,3-dinitrocrotonate, bp 66-69° (0.05 mm), n_D^{25} 1.4480, and 1.5 g of ethyl β -(2-fluoro-2,2-dinitroethoxy)acrylate, bp 95-100° (0.025 mm) (in a molecular still), n_D^{25} 1.4570.

Ethyl 3-Fluoro-3,3-dinitrocrotonate. - Fluorodinitromethane⁵ (5.0 g 0.04 mol) was added, with stirring, to a solution of 1.0 g of sodium hydroxide and 3.33 g (0.035 mol) of ethyl propiolate in 50 ml of water at 0-5°. After 45 min a cold solution of 2.0 g of sodium hydroxide in 20 ml of water was added and the mixture was stirred for an additional 45 min. The product was extracted with 35 ml of methylene chloride and distilled to give 2.0 g (26% yield) of colorless liquid, bp 65-66° (0.1 mm), n_D^{25} 1.4481.

Anal. Calcd for $C_6H_7N_2FO_6$: C, 32.9; H, 3.2; N, 12.6; F, 8.6
Found: C, 32.5; H, 2.9; N, 12.3; F, 8.9.

The infrared spectrum showed absorption peaks at (μ): 3.20(vw); 3.31(w); 3.40(w); 5.77(s); 6.20(s); 6.80(w); 6.90(w); 7.09(m); 7.20(m); 7.60(s); 8.05(s); 8.36(s); 9.40(m); 9.77(m); 10.25(w); 11.27(w); 12.10(w); 12.40(w); and 12.60(m).

Nmr spectra (no solvent) indicated a 1:2.5 ratio of trans to cis isomers. The fluorine spectrum showed a doublet ($J = 18$ cps) at ϕ^* 109 for the trans isomer and a broadened peak at ϕ^* 93 for the cis isomer. The proton spectrum showed for the trans isomer, a quarter ($J = 7.3$ cps) at δ 4.34 for the methylene, a triplet at δ 1.35 for the methyl, and a doublet of doublets ($J_{HH} = 15.6$ cps, $J_{HF} = 18$ cps) at δ 7.3 for the β -olefinic hydrogen. The α -olefinic hydrogens and both olefinic hydrogens of the cis isomer overlapped at δ 6.5 - 7.05. The cis isomer methylene appeared as a triplet

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($J = 7.3$ cps) at $\delta 4.33$, and the methyl appeared at $\delta 1.35$.

Dimethyl 2-Fluoro-2,2-dinitroethoxyfumarate - A mixture of 7.7 g (0.050 mol) of 2-fluoro-2,2-dinitroethanol and 7.1 g (0.050 mol) of dimethyl acetylenedicarboxylate was added dropwise at $3 - 5^\circ$ over a 15 min period with stirring to a solution of 7.9 g (0.10 mol) of pyridine in 75 ml of methylene chloride. The mixture was kept at $0 - 5^\circ$ for an additional 60 min and then was washed with a cold solution of 11 g of sulfuric acid in 50 ml of water. The methylene chloride solution was dried and stripped of solvent. Molecular distillation at $100 - 105^\circ$ (0.05 mm) gave 13.0 g (88% yield) of an oil which solidified at room temperature, mp $42 - 44^\circ$.

Anal. Calcd for $C_8H_9N_2FO_9$: C, 32.4; H, 3.0; N, 9.4; F, 6.4.
Found: C, 32.1; H, 3.1; N, 9.2; F, 6.4.

The infrared spectrum showed the following peaks (μ):
3.24(w); 3.34(w); 3.39(w); 3.45(w); 4.01(w); 5.80(s); 6.1(m); 6.22(s); 6.98(s);
7.5(m); 7.6(m); 7.88(m); 8.9(s); 9.08(s); 10.0(w); 10.4(m); 11.82(m); and 12.6(s).

The proton nmr spectrum ($CDCl_3$ solution) exhibited methoxy singlets at $\delta 3.75$ and $\delta 3.85$, a doublet at $\delta 5.3$ ($J_{HF} = 17$ cps) for the methylene and a singlet at $\delta 6.41$ for the methine. The fluorine spectrum showed a triplet ($J = 17$ cps) at $\phi^* 111.5$.

Dimethyl 2-Fluoro-2,2-dinitroethoxyfumarate and Dimethyl 2-Fluoro-2,2-dinitroethoxymaleate - To a solution of 5.0 g (0.125 mol) of sodium hydroxide in 150 ml of water was added, at $0 - 5^\circ$, 15.4 g (0.10 mol) of 2-fluoro-2,2-dinitroethanol and 14.2 g (0.10 mol) of dimethyl acetylenedicarboxylate. The reaction mixture was stirred at ambient temperature for four hrs, while 10%

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sodium hydroxide was added periodically to maintain pH 9-11. The product was extracted with 70 ml of methylene chloride, dried over sodium sulfate, and distilled to give 3.2 g (11% yield) of a colorless liquid, bp 128 - 130° (0.2 mm) n_{D}^{25} 1.4595.

Anal. Calcd for $C_8H_9N_2FO_9$: C, 32.4; H, 3.0; N, 9.4; F, 6.4.

Found: C, 31.8; H, 2.8; N, 9.6; F, 5.8.

The proton nmr spectrum ($CDCl_3$ solution) was consistent with a 3:1 ratio of dimethyl 2-fluoro-2,2-dinitroethoxyfumarate to maleate. The latter showed a $FC(NO_2)CH_2$ -doublet at δ 5.2, a broadened singlet at δ 5.6 for the olefinic proton, and a singlet at δ 3.8 for the methoxy group. The fluorine spectrum showed a triplet ($J_{HF} = 16$ cps) at ϕ^* 109.8. The distillation residue consisted of 10 g of viscous oil, with elemental analysis identical with that of the distilled material. The fluorine nmr spectrum showed a multiplet at ϕ^* 110.5 and the proton spectrum showed superimposed doublets at δ 4.8 and multiplets at δ 3.7 to 3.9.

Ethyl 4,4-Dinitro-2-pentenoate - A solution of 4.4 g (0.11 mol) of sodium hydroxide in 30 ml of water was added dropwise with stirring at 10° to a suspension of 12.0 g (0.10 mol) of 1,1-dinitroethane and 4.9 g (0.050 mol) of ethyl propiolate in 90 ml of water. After 18 hrs at ambient temperature, the product was extracted with 20 ml of methylene chloride and was distilled to give 1.8 g (~15% yield) of a pale-yellow viscous oil, bp 88 - 89° (0.1 mm), n_{D}^{25} 1.4670.

Anal. Calcd for $C_7H_{10}N_2O_6$: C, 38.5; H, 4.6; N, 12.8. Found: C, 38.2; H, 4.4; N, 12.3.

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The nmr spectrum (CCl_4 solution) was consistent with a 3:1 ratio of cis to trans ethyl 4, 4-dinitro-2-pentenoate. The olefinic protons appeared as pairs of doublets at δ 7.28 and 6.37 ($J = 15.8$ cps) for the trans isomer and at δ 6.92 and 6.27 ($J = 12.3$ cps) for the cis isomer. The ethoxy groups showed quartets at δ 4.17, $J = 7.1$ cps (cis) and δ 4.24, $J = 7.1$ cps (trans) and triplets at δ 1.25 (cis) and δ 1.29 (trans). Singlets at δ 2.42 (cis) and δ 2.37 (trans) were assigned to $\text{CH}_3\text{C}(\text{NO}_2)_2^-$.

Ethyl β -(2, 2-Dinitropropoxy)acrylate - Pyridine (5.0 g) was added at $22 - 25^\circ$ dropwise with stirring to a solution of 7.5 g (0.050 mol) of 2, 2-dinitropropanol and 4.9 g (0.050 mol) of ethyl propiolate in 60 ml of methylene chloride, and the reaction mixture was allowed to stand at ambient temperature for 18 hrs. The solution was washed with 150 ml of 8% aqueous sulfuric acid, and the solvent was removed. Molecular distillation at $115 - 120^\circ$ (0.025 to 0.05 mm) gave 9.8 g (79% yield) of light yellow liquid, n_D^{25} 1.4750.

Anal. Calcd for $\text{C}_8\text{H}_{12}\text{N}_2\text{O}_7$: C, 38.7; H, 4.8; N, 11.3. Found: C, 38.6; H, 4.9; N, 11.2.

The nmr spectrum (CCl_4 solution) indicated a 3.4:1 ratio of trans to cis isomers. The ethoxy methyl groups appeared as overlapping triplets at 1.23, and the ethoxy methylenes showed quartets at δ 4.11 ($J = 7.0$ cps) for trans and δ 4.06 ($J = 7.2$ cps) for cis. The $\text{CH}_3\text{C}(\text{NO}_2)_2^-$ signals overlapped at δ 2.28 and singlets at δ 4.81 (trans) and 4.90 (cis) were assigned to $-\text{CH}_2\text{-C}(\text{NO}_2)_2^-$. Doublets at δ 6.62 ($J = 6.9$ cps), 4.92 ($J = 6.9$ cps), 5.41 ($J = 12.4$ cps) and 7.53 ($J = 12.4$ cps) were assigned to the cis- α , cis- β , trans- α and trans- β olefinic protons, respectively.

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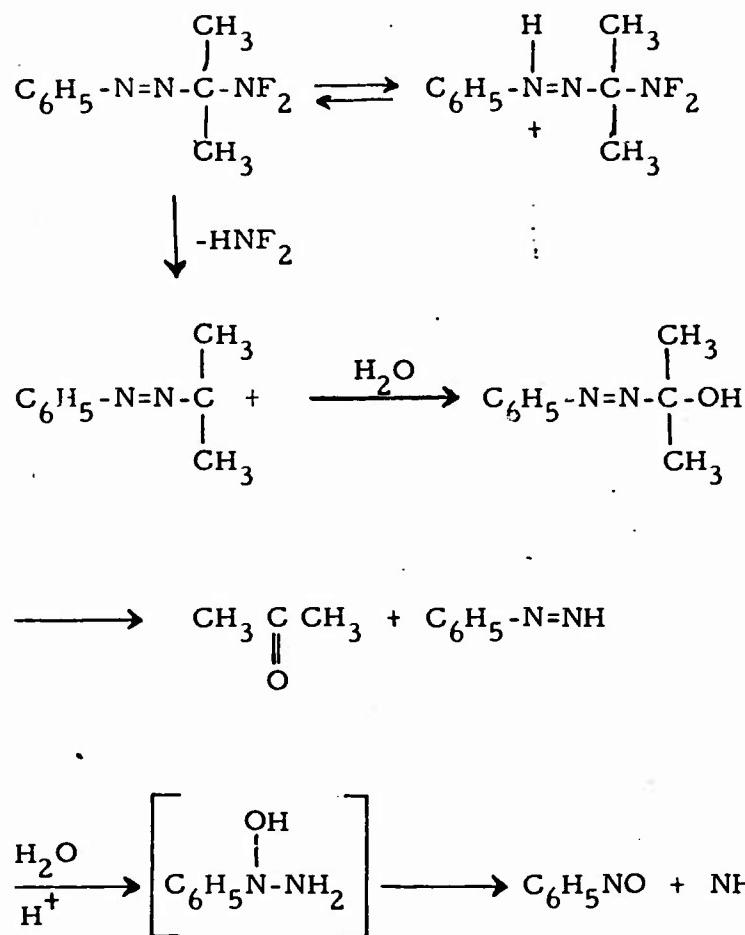
APPENDIX

NF CATIONS

(C) 2-Difluoramino-2-(phenylazo)propane was prepared previously by the reaction of 2-nitro-2-(phenylazo)propane with difluoramine in sulfuric acid.¹ The reaction of this difluoramino compound with strong acids offers the possibility of synthesizing novel cationic NF species, and this possibility is being explored by nmr spectroscopy.

(C) Solutions of the azo compound in concentrated sulfuric acid were prepared at 0°. Proton nmr spectra of freshly prepared solutions showed a broadened methyl peak at δ 2.04 and a complex aromatic multiplet at δ 7.6 to 8.4. Fluorine spectra showed only a singlet at ϕ -34.1. A reaction of the initial product took place, with a half-life of 4 hrs at room temperature. The δ 2.04 peak disappeared, and a new methyl singlet appeared at δ 2.95 and a 1:1:1 triplet ($J = 54$ cps) appeared at δ 5.87. The new peaks were shown to be due to acetone and ammonium ion, respectively, by the addition of samples. The color of the sulfuric acid solution changed on standing from pale yellow to a deep green, characteristic of nitrosobenzene.

(C) The spectra of the fresh solutions are consistent with simple protonation of the starting material. Subsequent hydrolysis would give difluoramine, acetone, and phenyldiimide. Hydration of the latter would give nitrosobenzene and ammonium ion.



(C) 2-Difluoramino-2-phenylazopropane exhibited a different type of reactivity in the stronger acid fluosulfonic acid. Solutions were prepared at -78° , and nmr spectra were determined at ambient temperature. The proton spectrum showed an aromatic multiplet and two doublets at δ 2.95 and 3.00, with slightly unequal coupling constants of about 1 cps. The fluorine spectrum showed a broadened singlet at ϕ +182.6. The nonequivalence of the two methyls and the magnitude of the coupling constants are

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consistent with fluorimonium ion structures.^(2, 3) The F¹⁹ chemical shift of fluorimonium ions, however, have been observed to have large negative values. A conclusive structure assignment cannot be made at this time.

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